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Porcelain tiles by the dry route

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In Brazil, the second largest tile producer of the world, at present, 70% of the tiles are produced by the dry route. One of the main reasons that lead to this development is the fact that the dry route uses approximately 30% less thermal energy them the traditional wet route. The increasing world concern with the environment and the recognition of the central role played by the water also has pointed towards privileging dry processes. In this context the objective of the present work is to study the feasibility of producing high quality porcelain tiles by the dry route. A brief comparison of the dry and wet route, in standard conditions industrially used today to produce tiles that are not porcelain tiles, shows that there are two major differences: the particle sizes obtained by the wet route are usually considerably finer and the capability of mixing the different minerals, the intimacy of the mixture, is also usually better in the wet route. The present work studied the relative importance of these differences and looked for raw materials and operational conditions that would result in better performance and glazed porcelain tiles of good quality.

Keywords: porcelain tiles, dry route, granulometry and fusibility.

Revestimientos porcelánicos obtenidos por vía seca

En Brasil, en este momento segundo productor mundial, el 70% de los pavimentos cerámicos se obtiene por vía seca. Una de las razones fundamentales se debe a que esta vía supone un consumo energético inferior, en un 30%, a la via húmeda tradicional. La creciente preocupación mundial sobre los problemas medioambientales y el reconocimiento de l papel central que juega el agua en este proceso han favorecido el desarrollo de la vía seca. En este contexto, el objetivo del presente trabajo es estudiar la viabilidad de la producción de pavimentos porcelánicos de alta calidad por vía seca. Una breve comparación entre ambas vías, en las condiciones standard de producción vigentes para producciones que no son de porcelánico, indican que existen dos diferencias substanciales; el tamaño de partícula, utilizado en la vía húmeda es considerablemente mas fino,y la capacidad de mezclado entre los diferentes minerales que integran la composición es normalmente tambien mejor en la vía húmeda. El trabajos analiza la importancia relativa de ambos factores y estudia las materias primas y condiciones de proceso que podrían conducir a la obtención de pavimentos esmaltados de buena calidad

Palabras clave: revestimientos porcelánicos, vía húmeda, vía seca, granulometría, fusibilidad

1. INTRODUCTION

The "dry route" can be considered the greatest technological innovation of the Brazilian ceramic tile industry [1]. In the last five years the Brazilian production of ceramic tiles has presented incredible growth rates. The fast growth of the production of dry route products, that represents almost 70% of the Brazilian production, was responsible for this achievement. The quality of the dry route products has also improved considerably and at present the large majority of the products attends all the requirements of the international standards and it's very hard to distinguish tiles produced by the dry and wet route.

Among the various typologies of tiles, the production of porcelain tiles [2] deserves special attention, first because it has added considerable value to ceramic tiles and second because it has penetrated consumer classes that usually would prefer more noble products such as natural stones. The increase in the production of porcelain tiles has also taken place in Brazil where it's produced by the traditional wet route.

So, considering all the information presented above and two of the most appealing characteristics of the dry route, it consumes approximately 30% [7] less thermal energy and it's environmentally friendly because it doesn't use water in the body preparation, it's worth studying the possibility of producing good quality porcelain tiles by the dry route.

Considering the major differences between the wet and dry route processes, there are some major technological barriers to be overcome for the production of good quality porcelain tiles by the dry route:

1. The **particle size** produced by the wet route is considerably finer than the one produced by the dry route in the operation conditions typically used to produce BIIb products in Brazil;

2. The **degree of mixture** of the various minerals present in the different raw materials used in the body formulation, and consequently the homogeneity of the composition, achieved by the wet route is much better than the one obtained by the dry route [3];
3. The **granules** produced by spray-drying are more spherical and larger than those obtained by the dry route [4]. Consequently, the fluidity [5] of the granulated powder produced by the wet route tends to be considerably higher than the one produced by the dry route where the shape of the granules is much more irregular;
4. The **defects** developed as a consequence of the presence of undesirable minerals, such as calcite, are usually much more severe in the dry route process because in the operating conditions used to produce BIIb products the particles are considerably coarser [3];
5. The **roughness of the surface** [6] of the products manufactured by the dry route tends to be higher due to the coarser particles produced by the dry route.

The present work studied items 1 and 2 listed above with the objective of identifying alternatives to overcome or minimize these barriers. To achieve this objective the experimental work was subdivided in three parts, as presented in the following item.

2. EXPERIMENTAL PROCEDURE

2.1 Relevance of the particle size and degree of mixture

A body composition (Table I), originally used to manufacture glazed porcelain tiles by the wet route, was prepared by three different routes in the laboratory:

- Wet route: the composition was ground in a laboratory ball-mill with the addition of water and sodium silicate, as deflocculant, until less than 5.0% was retained in an ASTM #325 sieve (aperture of 45µm). Then, the slurry was dried and granulated with the addition of 7.0% of water;
- Dry route: the composition was dry-ground in a hammer mill and mortar until it passed through the ASTM #45 sieve (aperture of 350µm). This condition produces particle size distributions similar to those found in Brazilian industries producing BIIb tiles by the dry route. After grinding, the powder was granulated with addition of 7.0% of water;
- Mixed route: the raw materials were individually wet-ground until less than 5.0% was retained in an ASTM # 325 sieve (aperture of 45µm). After grinding, the individual raw materials were dried, dosed according to the composition (Table I) and mixed by the dry route. The composition prepared by this procedure presented approximately the same particle size distribution of the one prepared by the wet route, however, the degree of mixture was similar to the obtained by the one prepared by the dry route. The mixture of raw materials was granulated with addition of 7.0% of water;

Table I. Raw materials and body composition

Raw materials	Composition (%)
Clay P	19.6
Clay ME	3.5
Clay SH	4.7
Sodic feldspar	23.4
Filito FT1	28,1
Filito FT 5	13.2
Talc TC2	7.5

The particle size distribution of the three powders were determined by sedimentation and wet sieving, for the coarser fractions.

The compositions prepared by the procedures described above were characterized comparatively. The samples were prepared by pressing and the apparent density after drying was around 1.90 g/cm^3 for the three samples. After drying the samples were fired at different temperatures in cycles of about 45 minutes. The water absorption and shrinkage of the samples were measured.

2.2 Effects of the particle size on the dry route

The composition presented in Table I was prepared in a laboratory hammer mill and mortar in order to produce different particle sizes with the same chemical composition:

- 100% passing through a 45 ASTM sieve (aperture of 350µm);
- 100% passing through a 80 ASTM sieve (aperture of 180µm);
- 100% passing through a 140 ASTM sieve (aperture of 105µm);
- 100% passing through a 230 ASTM sieve (aperture of 63µm);

The particle size distribution, sample preparation, processing conditions and characterization, were the same as described in the previous section.

To complement the study of the effects of the particle size on the dry route, the thermal expansion coefficient and the pyroplasticity index were measured for samples fired at the temperatures of maximum densification rates.

2.3 Body compositions compatible with the dry route

Compositions containing other raw materials, different from those presented in Table I, more compatible with the characteristics of the dry grinding, were studied. The general guidelines for the selection of the raw materials were:

- Clays with low moisture content, only subjected to the action of atmospheric agents, to avoid the need for a prior drying step;
- Formulations with low or zero content of hard raw materials, that would increase the wear of the mills and decrease their productivity;

- Compositions with fewer components with similar characteristics, to avoid heterogeneities as a consequence of the lower mixing capability typical of the dry route.

The compositions described in Table II were evaluated after dry milling (hammer mill and mortar) with particle sizes below 63μm (100% passing through 230 ASTM sieves). The following characteristics were measured for the different samples:

- Compaction curves: for the compositions with fixed moisture content of 8.0%, compaction pressures between 150 and 400 Kgf/cm^2;
- Modulus of rupture (bending test) after drying: by the three-point bending test for the samples pressed at different compaction pressures;
- Gresification curves: determined after firing in cycles of about 45 minutes, with maximum temperature between 1140 and 1220^{o}C;
- Modulus of rupture (bending test) after firing: by the three-point bending test for samples fired at temperatures used for the gresification curves;
- Pyroplastic index, coefficient of thermal expansion and color and texture after firing (visual and colorimetric analysis in spectrophotometer) for the samples fired at the maximum densification temperature determined by the gresification curves of each composition.

TABLE II. COMPOSITIONS OF THE TESTED PORCELAIN TILES VIA DRY ROUTE

Raw materials	P10	P11	P12
White clay	40	45	45
Filito	45	45	40
Red clay 1	-	10	-
Red clay 2	-	-	10
Talc	5	-	5
Sodic Feldspar	10	-	-

3. RESULTS AND DISCUSSIONS

3.1 Relevance of the particle size and degree of mixture

Figure 1 shows the particle size distribution for the powders prepared by the three different processes. As expected, particle size distributions of the compositions prepared by the "wet" and "mixed" routes were very similar. However the composition prepared by the dry route presented a much wider particle size distribution, with a larger content of coarser particles.

Figure 2 shows the gresification curves of the samples prepared by the three routes. The results indicate that the fusibility of the mixtures was highly influenced by the preparation method. Additionally, it was found that the gresification curves of the samples prepared by the "wet" and "mixed" routes were quite similar. However, the sample prepared by the dry route presented a lower fusibility and consequently required a much higher temperatures to achieve the water absorption necessary to characterize a porcelain tile. These results indicate that, from the point of view of the behavior on firing, the particle size is considerably more relevant than the degree of mixture. However, from the point of view of the visual aspect, also a very important characteristic, the degree of mixture do play an very important role and the samples prepared by the dry route presented, from the point of view of the color homogeneity, a very heterogeneous surface with pigmentations visible to the naked eye and a slightly coarser texture.

3.2 Effects of the particle size on the dry route

The results of the previous section have shown that, from the point of view of the behavior on firing one should look for fine particles, however the production of finer particles reduces considerably the output of the mill. So, one should look for particles that are fine enough trying to avoid loosing the productivity of the mill and the pigmentation of the ceramic body. In this scenario it's necessary to study the effects of the particle size on the dry route to determine how fine should be the powder to produce the necessary fusibility

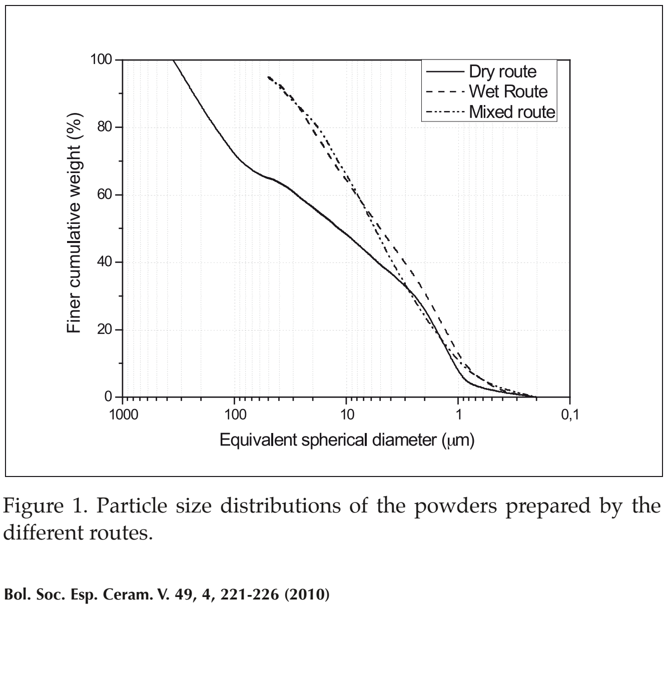

Figure 1. Particle size distributions of the powders prepared by the different routes.

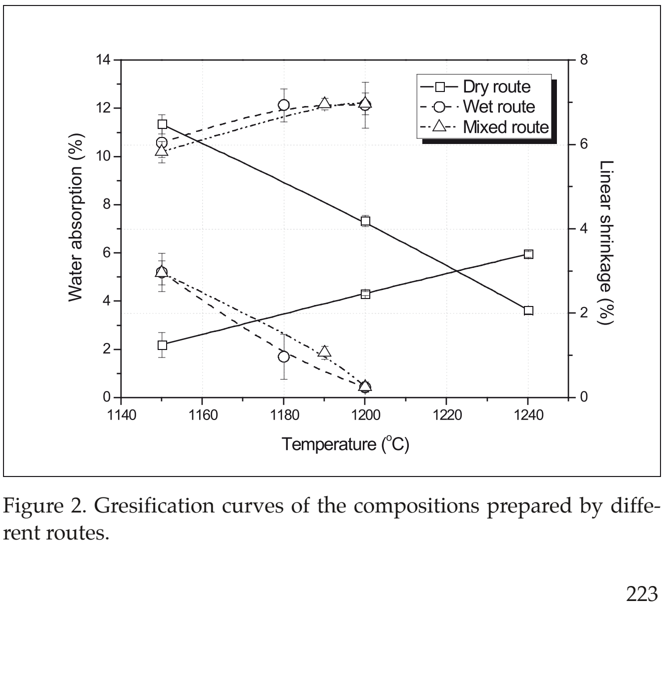

Figure 2. Gresification curves of the compositions prepared by different routes.

TABLE III. PARTICLE SIZES AND DE CORRESPONDENT THERMAL EXPANSION COEFFICIENTS AND PYROPLASTIC INDEX FOR SAMPLES PREPARED BY THE DRY ROUTE.

Composition mixture	α_{25-325} (°C^{-1})	I.P. (cm^{-1})
100% < 350 μm	58.3 x 10^{-7}	18.5 x 10^{-5}
100% < 180 μm	56.8 x 10^{-7}	17.5 x 10^{-5}
100% < 105 μm	59.7 x 10^{-7}	14.4 x 10^{-5}
100% < 63 μm	65.6 x 10^{-7}	9.4 x 10^{-5}
Wet route	66.2 x 10^{-7}	7.6 x 10^{-5}

without the pigmentation of ceramic body. It's important to mention that the production of finer particles usually results in a considerable loss of productivity of the dry mill, so it's necessary to determine the maximum particle size that will permit to take advantage of the characteristics of the dry route, mentioned earlier, without compromising the aesthetics of the final product. That's the objective of this part of the work.

The dry grinding process was adjusted to produce powers with the same chemical and mineralogical compositions and different particle size distributions (Figure 3). For comparative purposes, Figure 3 also shows the particle size distribution of the composition prepared by the wet route. The samples with particles smaller than 105 and 63 μm have size distributions similar to the one prepared by the wet route.

The gresification curve of the dry-milled sample containing particles smaller than 63μm is very similar to the curve corresponding to sample prepared by the wet route, in Figure 4. Satisfactory results were also obtained by the sample containing particles smaller than 105μm, although a slowdown of the gresification process can be observed. Samples containing coarser particles presented strong pigmentation and lower fusibility requiring higher temperatures to reach the necessary water absorption.

Table III shows the thermal expansion coefficients and pyroplasticity index of the samples with different particle sizes. The thermal expansion coefficients cannot be too low to

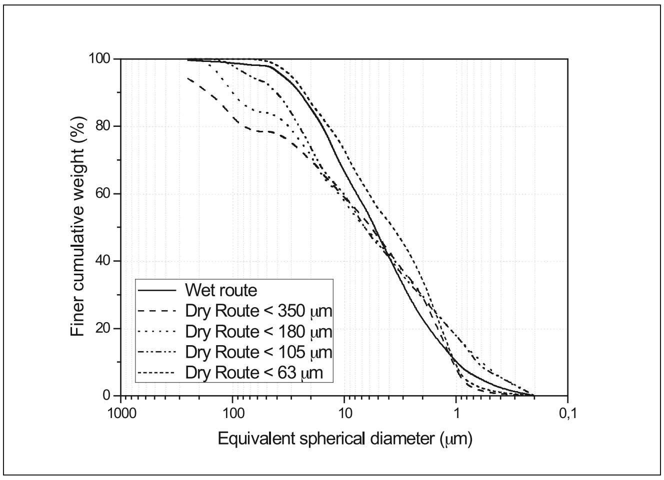

Figure 3. Particle size distributions of the dry-milled samples.

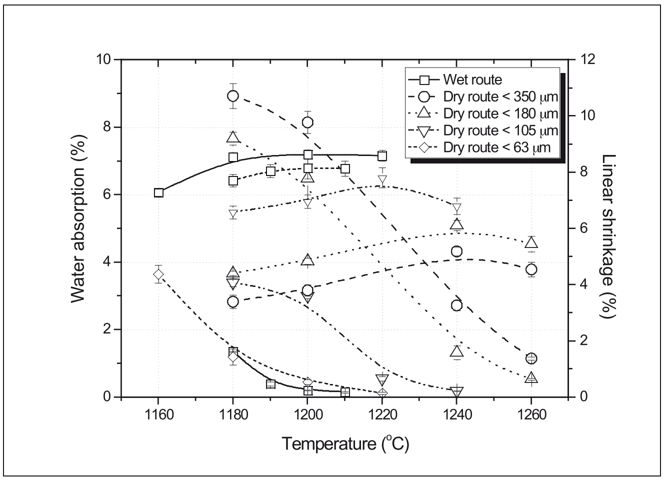

Figure 4. Gresification curves of samples with different particle sizes prepared by dry milling.

TABLE IV. CHARACTERISTICS OF THE STUDIED COMPOSITIONS.

Characteristics	Wet route	P10	P11	P12
Bulk density 110°C (g/cm^3)	1.91	1.95	1.92	1.90
Mechanical strength 110°C (MPa)	3.7	2.4	2.8	4.2
Maximum temperature densification (°C)	1190	1200	1200	1190
Loss of ignition (%)	4.9	4.8	4.2	4.5
Water absorption (%)	< 0.5	< 0.5	< 0.5	< 0.5
Firing linear shrinkage (%)	7.2	8.2	8.0	8.3
Mechanical strength T_{max} (MPa)	51	48	48	52
Thermal expansion – α_{25-325} (°C^{-1})	68.2	64.6	66.1	65.6
Pyroplasticity index (cm^{-1})	7.6	6.9	5,7	6.4
Chromatic coordinates - L*, a*, b*	57.2	56.7	53.3	53.1
	1.2	1.4	3.4	2.0
	12.5	12.0	12.3	11.4

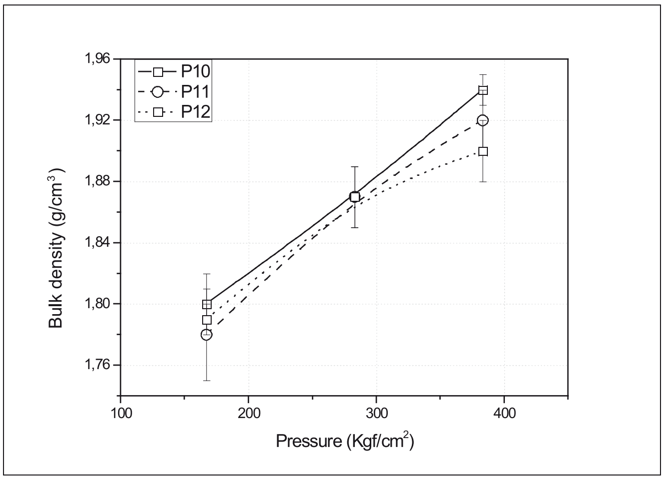

Figure 5. Compaction curves of the compositions of porcelain bodies prepared by the dry route.

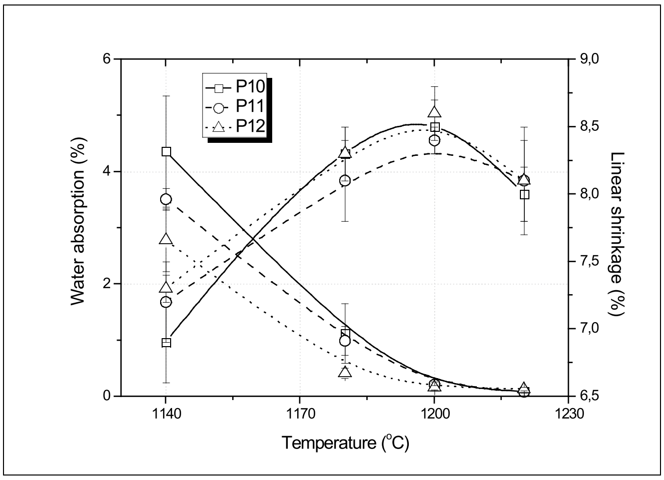

Figure 6. Gresification curves for formulations of porcelain tiles produced by the dry route.

allow the development of compatible glazes that will result in acceptable curvatures in the final product. Also the pyroplastic index should be reduced to prevent distortions on firing.

It was observed that the coarser samples, fired at higher temperatures, necessary to reach the required water absorption, presented a higher pyroplasticity index (IP) and lower thermal expansion coefficients. These differences are probably due to the decrease of the glass viscosity at higher temperatures, that would favor the pyroplastic deformation, and the increase of the crystalline quartz dissolved in the melted liquid, that would result in a decrease of the thermal expansion coefficient.

So, one can conclude that good fusibility without pigmentation, for the studied compositions, can be achieved with particles smaller than 63μm and satisfactory results are possible for particles smaller than 105μm.

3.3 Body compositions compatible with the dry route

In this part of the work new raw materials, different from the ones presented in Table I, more compatible with the characteristics of the dry route were used.

Figure 5 shows the compaction curves of the three different compositions formulated for this part of the work. The results indicate that the apparent density of the three compositions have increased with increasing pressure and reach acceptable densities for compaction pressures similar to those practiced in the manufacture of glazed porcelain tiles. It is observed that composition P10 achieved a higher apparent density, probably due to the presence of feldspar that introduced coarser particles.

Table IV shows that these compositions also have satisfactory mechanical behavior before firing. The dry modules of rupture of the three compositions prepared by the dry route are similar to the composition prepared by the wet route, characterized for comparison.

Figure 6 shows the gresification curves of the compositions. All the compositions tested presented maximum densification around 1200°C and reached water absorptions smaller than 0.5% at temperatures between 1180 and 1190°C in firing cycles of 45-minute. The presence of feldspar in composition P10 didn't result in a higher gresification rate. Composition P12, consisting solely of clays, filito and talc was the less refractory among the formulations tested. The development of feldspar-free formulations may be interesting for the dry route process, since due to the hardness of feldspars, it is expected that compositions free of such raw material show greater milling efficiency and less equipment wear.

The other properties of the compositions during and after firing are presented in Table IV, together with the values obtained by glazed porcelain tile prepared by the wet route method.

Comparing the results of the dry route compositions in Table IV, one can see that there are some subtle differences in color, thermal expansion, pyroplasticity and dry mechanical strength. In general, the properties of the compositions prepared by the dry route are very similar to the properties of the compositions prepared by the wet route.

4. CONCLUSIONS

Based on the results, the following conclusions can be stated:

- Satisfactory results were obtained in laboratory scale for the production of light color (whitish) glazed porcelain tiles prepared by the dry route;
- Particle size is more relevant than the degree of mixture for the gresification process of powders prepared by the dry route;
- It is not possible to obtaining light color (whitish) porcelain tiles with the particle sizes currently used in the Brazilian dry route plants. It's necessary to obtain particles smaller than 105μm or preferably smaller than 63μm to obtain satisfactory results;
- It is possible to develop porcelain tile compositions more compatible with the characteristics of the dry route process. The appropriate selection of the raw materials will result in products that fulfill all the necessary technical characteristics and take advantage of the high productivity and environmental aspects of the dry route.

5. AKNOWLEDGMENTS

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